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FOR   ACID GAS ENRICHMENT PROCESS

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Dear Sir:

In response to the Notice of Allowance dated June 28, 2006, please find enclosed herewith a certified copy of Canadian application, Serial No: 2,405,719 upon which convention priority is claimed. Would you please make this of record in this application.

Respectfully submitted

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Specification and Drawings, as originally filed, with Application for Patent Serial No: **CA 2405719**, on September 27, 2002, by **GARY PALMER**, for "Acid Gas Enrichment Process".

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Agent certificateur/Certifying Officer

July 11, 2006

Date

Canada

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TITLE: **ACID GAS ENRICHMENT PROCESS**

5   FIELD OF THE INVENTION

The present invention relates to treatment of natural gas generally, and in particular relates to processes for enriching acid gases for sulphur plant feeds.

BACKGROUND OF THE INVENTION

10   a)   Industry Background

Petroleum reservoirs, whether primarily oil reservoirs or gas reservoirs, often contain significant quantities of hydrogen sulphide (H_2S) and carbon dioxide (CO_2) in addition to hydrocarbons. These contaminants must be removed or at least reduced to meet commercial specifications for purity before the natural gas can be marketed to 15   consumers. The hydrogen sulphide and carbon dioxide, usually referred to as "acid gases", have commercial value as by-products in and of themselves if, for example, the hydrogen sulphide is converted to sulphur and the CO_2 is used for miscible flooding of oil reservoirs. Otherwise, the acid gases are considered to have no marketable value, and are disposed of either by pumping down a disposal well or by flaring.

20   Commercial specifications for natural gas require that essentially all of the hydrogen sulphide be removed from the gas, typically to a final concentration of 4 PPM

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(parts per million) by volume or less. Carbon dioxide must likewise be reduced, but being non-toxic, the tolerance for CO_2 is much higher (typically 2% by volume for commercial pipeline quality gas).

The extremely stringent specification for H_2S content in natural gas has dictated

5   the type of process that must be used, and virtually all natural gas being "sweetened" today is treated by one of the various alkanolamines that are available for this purpose. More than half a century ago, the Girbitol process was introduced in which the primary amine, monoethanol amine (popularly known as "MEA"), was used as the absorbent. Since then, other amines have become popular, namely diethanoamine (DEA), and a

10   current favourite, methyldiethanol amine (MDEA), which is popular because of its preferential affinity for hydrogen sulphide over carbon dioxide. In most cases, generic amine in an aqueous solution is used, although various processes are available in which chemical additives are used in the amine solution to enhance certain characteristics of the absorbent. Amine has gained widespread acceptance and popularity because it can

15   produce a natural gas product that reliably meets the strict requirements for gas purity, especially the requirements for hydrogen sulphide, and can do it relatively inexpensively.

Alternative processes for acid gas removal, such as physical absorption in a solvent or distillation for removal of acid gases, have not been used extensively, except possibly for bulk removal followed by cleanup with amine. Amine is able to remove acid

20   gas components by reacting with them, which in an equilibrium situation can potentially

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totally remove the acidic components from the gas. Acid gases can be removed by other processes based on chemical reaction, such as the hot carbonate process and various forms of the iron oxide process, which can meet the specifications for gas purity. However, for many practical reasons these processes have never gained widespread popularity.

Historically, the primary concern of the gas processing industry has been to produce natural gas that will meet the stringent requirements for gas purity imposed by pipeline and distribution companies who establish the specifications for natural gas. There has been much less attention directed toward the by-product of the amine process – the acid gas mixture of H_2S and CO_2 that is co-absorbed in the process. Typically, these two gases are not subjected to any separation process to recover them as two separate entities, but are sent directly as feed to a sulphur plant.

Most sulphur plants utilize some version of the Claus process in which one third of the H_2S is oxidized by combustion to SO_2, which then subsequently reacts with the remaining two thirds of the H_2S to produce elemental sulphur and water. The second acid gas component, carbon dioxide, is an inert gas and a none-participant in the chemical reaction, but because of the thermodynamics of the Claus process, carbon dioxide will detrimentally affect the reaction to produce sulphur. The presence of carbon dioxide dilutes the reactants – hydrogen sulphide, oxygen, and sulphur dioxide –, retarding the reaction and reducing the percentage conversion to sulphur. The dilution effect directly

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influences the chemical equilibrium of the Claus process, fundamentally reducing the attainment of high rates of sulphur conversion. In cases where the acid gas feed to the sulphur plant is rich in H_2S, the effect of dilution by CO_2 may not be too serious, but in those cases where the quantity of CO_2 exceeds the quantity of H_2S by a factor of five or

5   more, the effect on thermodynamic equilibrium conversion to sulphur is very significant.

A secondary effect of dilution of H_2S by excessive quantities of CO_2 is flame stability in the reaction furnace where H_2S is oxidized to SO_2. Carbon dioxide is an effective fire extinguishing chemical, and when present in excessive amounts in the reaction furnace it can inhibit combustion, and in some cases completely quench the

10   flame. The dilution effect of CO_2 in the firebox of the furnace will also reduce furnace temperature to the extent that complete combustion does not occur. This necessitates the addition of natural gas to the acid gas entering the sulphur plant in order to improve combustion and maintain flame temperature in the reaction furnace. Natural gas in the reaction furnace causes a further complication by increasing the undesirable reaction by-

15   products, carbonyl sulphide and carbon disulphide. These are the products of reaction between methane and other hydrocarbons, CO_2, H_2S and oxygen, and although they may be present in the furnace effluent in concentrations of less than 1%, they effectively bind up a portion of the sulphur which does not completely hydrolyze back to H_2S in the catalyst beds of the sulphur plant, thus reducing the overall conversion of H_2S to sulphur.

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It is apparent that there is a clear need for a process that will increase the concentration of H_2S in the feed gas entering a sulphur plant. Preferably the process should improve the conversion of H_2S to sulphur, and should also solve many of the operational problems associated with feed gases that are too lean in H_2S.

5   b)   Relevant Technology

Advances toward improvement of H_2S/CO_2 ratios in sulphur plant feed have generally been based on the selectivity of methyldiethanol amine (MDEA) for H_2S over CO_2 when in contact with sour gas. Tertiary amines such as MDEA and also di-isopropyl amine (DIPA) exhibit this preferential affinity for H_2S. Other amines such as MEA and

10   DEA tend not to exhibit significant preferential affinity, and will therefore strongly absorb both H_2S and CO_2.

In studying the relative affinities between tertiary amines and the acid gases hydrogen sulphide and carbon dioxide, two things must be considered. One is reaction equilibrium, which is defined as the final concentrations of reactants and reaction

15   products after sufficient time has elapsed to attain steady levels. Equilibrium in thermodynamic terms occurs when the total free energy of the mixture reaches a minimum. The second thing to consider is reaction kinetics, which refers to the rate at which a reaction occurs. While consideration of reaction equilibrium is important, in the practical application of industrial chemistry, consideration of reaction kinetics is equally

20   important since reaction time will greatly influence the final distribution of components

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in a reaction mixture. Such is the case with the tertiary amines, and also with DIPA. While the reaction with H_2S is rapid, the reaction with CO_2 is slow. Therefore, although consideration of reaction equilibrium alone would suggest that both H_2S and CO_2 could react almost to completion, when the reaction kinetics are considered, only the H_2S reaction approaches completion, while the CO_2 reaction goes only part way. Selective absorption of H_2S can therefore be improved by limiting contact time. The mechanical design of contacting equipment, the operating conditions, and the presence of special chemical promoters can all have a bearing on selectivity of tertiary amines for H_2S over CO_2.

The popular amines MEA, DEA, MDEA, DGA, and DIPA all have in common a trivalent nitrogen atom to which are attached alcohol radicals (either ethanol or propanol). For example, the primary amine, monoethanol amine, has one ethanol group and two free hydrogen atoms. The secondary amine, diethanol amine, has two ethanol groups (as the name suggests) and one hydrogen atom. DGA has a single ether-ethanol chain with two hydrogens. MEA, DEA, and DGA all react rapidly with carbon dioxide, combining with the available proton of the amine molecule to form a carbamate radical (see fig.1). DIPA, which has two propanol structures and a single hydrogen atom, is not fully substituted, and is therefore not a tertiary amine. DIPA does not exhibit the rapid reaction with CO_2 that is characteristic of the primary and secondary amines, each of which have an available proton. Apparently, the proton is not available for reaction with CO_2, so the

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carbamate reaction does not occur readily with DIPA. Methyl diethanol amine (MDEA) is a tertiary amine which has no proton attached to the nitrogen atom. As the name suggests, the three valences of nitrogen are occupied by two ethanol groups and one methyl group, so the carbamate reaction, which requires a labile proton, cannot occur.

5   The reaction between a molecule of MDEA and a molecule of CO_2 is somewhat more complex. When a CO_2 molecule is dissolved in an aqueous solution, due to its acid nature it hydrolyzes to form carbonic acid (H_2CO_3). In a process which occurs slowly, the carbonic acid then dissociates to form positive hydrogen ions and negative bicarbonate ions. The bicarbonate may, to some extent, dissociate further to form

10   additional positive hydrogen ions and negative carbonate ions. The MDEA molecule, being mildly basic in character, will bond loosely with the available hydrogen ions to form a positively charged amine-hydrogen ion that coexists in solution with negatively charged bicarbonate and carbonate ions (see fig. 2). Since the carbonic acid dissociation step is relatively slow kinetically, the overall sequence of steps must also proceed slowly.

15   The overall kinetic acid-base reaction between tertiary amines and carbon dioxide must therefore occur quite slowly. In contrast, the acid-base reaction of hydrogen sulphide occurs rapidly. In typical contacting devices, the H_2S reaction rate is at least ten times faster than the CO_2 reaction. These differential rates of reaction help to explain the selectivity of tertiary amines for H_2S over CO_2.

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As the reaction between the amine and acid gas proceeds, more of the available amine molecules become bound to acid gas molecules, leaving fewer unreacted amine molecules available to react with the acid gas. This lack of available reactive amine molecules in the presence of acid gas slows the rate of reaction. Solution loading is therefore another factor influencing the selectivity of tertiary amines for H_2S.

Reaction kinetics, however, are only one factor to consider in analyzing the absorption of acid gases by amine solutions. As in physical absorption, acid gas molecules must migrate to the gas liquid interface under the action of the concentration gradient that exists in the gas film adjacent to the interface. The molecule must then penetrate the interface and migrate inward until an unreacted amine molecule is encountered. As the mass transfer of acid gas molecules from the bulk gas phase into the liquid phase occurs by diffusion, the process of transfer requires a finite amount of time. Diffusion in this case occurs in two sequential steps. First, diffusion through the gas phase occurs near the interfacial boundary at the gas diffusion rate and, second, diffusion through the liquid phase occurs near the liquid boundary of the interface at the liquid diffusion rate. As a significant factor in rate limitations for tertiary amines, mass transfer by diffusion must be considered in addition to chemical rates of reaction. It has also been observed that selectivity for H_2S increases as contact pressure decreases.

As previously mentioned, H_2S reacts almost instantly with amine, so mass transfer by diffusion through the gas phase is the rate-limiting step for hydrogen sulphide. For

carbon dioxide, the dissociation to form hydrogen and bicarbonate ions proceeds so slowly that the concentration gradient in the liquid phase that drives the mass transfer is impeded. This impedance constitutes an additional resistance to absorption of CO_2.

Practical applications for the selectivity of tertiary amines for H_2S over CO_2 have, for the most part, been limited to absorption of acid gases from natural gas in a primary absorber (see fig.3 which shows a standard arrangement). Circulation rate and residence time in the absorber permit a portion of the CO_2 to remain unabsorbed while H_2S is totally removed from the gas. Commercial specifications for natural gas require near to total removal of H_2S, but in most cases up to 2% carbon dioxide in the purified gas is acceptable. The tertiary amine, methyldiethanol amine (MDEA), is usually the preferred absorbent. The practice of partially removing CO_2 from the natural gas is referred to as "slipping" the CO_2.

In the technical record, references to MDEA's preferential affinity for H_2S over CO_2 appear as early as 1950, when Frazier and Kohl first noted the phenomena (see Frazier, H. D. and A. L. Kohl, "Selective Absorption of Hydrogen Sulfide from Gas Streams", Ind. Eng. Chem., 42, 2288-2292 (1950)). Since then, the technical literature has traced the development of design methods for the use of MDEA. By the 1980's MDEA had gained widespread use in the gas industry, but applications were generally restricted to the relatively simple operation of slipping a portion of the CO_2 in the high pressure absorber while totally absorbing the H_2S. The formidable challenges of

quantitatively predicting the combined chemical reaction and mass transfer relationships were not met until recent years, and although present methods are adequate, there is still significant room for improvement.

Present methods involve computational procedures to establish both chemical

5   and mass transfer equilibrium relationships between the amine and the acid gases. The concentrations of the various chemical species seek to arrive at final equilibrium concentrations at which point no further change will occur. It is the difference between actual concentrations and equilibrium concentrations that provides the driving force for change to occur. Because there are various resistances to these changes, change does not

10   occur instantaneously; it occurs at a definite rate determined by the nature of the components, and by circumstance. Rate of change is proportional to driving force but inversely proportional to resistance, so if driving force and resistance can be calculated, the rate of change can also be calculated. If infinite time were available, equilibrium concentrations would eventually be attained. In reality, however, time constraints dictate

15   that only a partial approach to equilibrium is attainable. This procedure forms the basis for the design of processing equipment to preferentially absorb H_2S from gases containing a mixture of both H_2S and CO_2.

Since H_2S proceeds toward equilibrium rapidly, it approaches equilibrium more closely than CO_2, which proceeds slowly. In real absorbers, equilibrium can be

20   approached, but is never attained. In a multistage contacting device such as a trayed

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tower, if each actual stage had sufficient time to reach equilibrium, the stages would be said to be 100% efficient. This hypothetical scenario provides a measure of the change that takes place on each actual stage if the actual change is expressed as a percentage of the change that would take place if equilibrium were attained. The actual change taking

5   place on the stage could then be calculated from the known (100%) efficiency of the stage when equilibrium is attained. For example, in a typical trayed MDEA absorber, the tray efficiency for H_2S is approximately 50%, whereas the tray efficiency for CO_2 is typically about one-tenth as much, or 5%. If this preferential effect is factored into multiple stages of contact, the separation of H_2S from CO_2 can be significant. In practical situations,

10   however, it must be recognized that the final concentration of H_2S in the treated gas must be very low, while the concentration of CO_2 is many times higher. The driving force for absorption of H_2S is low, while the driving force to absorb CO_2 is relatively high in the top trays of the absorber tower. This means that, in the process of absorbing essentially all of the H_2S, significant quantities of CO_2 will inevitably also be absorbed, and that the

15   rich MDEA exiting from the bottom of the absorber column will contain a large amount of CO_2 along with the absorbed H_2S.

Over the years various schemes have been proposed to improve the selectivity of tertiary amines for H_2S over CO_2, but unless the true complexity of the absorption process is recognized, the success of these schemes will be compromised. For example, many

20   schemes attribute to the tertiary amines a strong similarity to physical absorption, in

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which acid gases are absorbed or desorbed in response to changes in pressure or temperature. Physical absorbents generally follow the principle of Henry's Law, which states that the concentration of a distributed component in the liquid phase is proportional to the partial pressure of the component in the gas phase. Due to chemical reactions that

5   inevitably occur in the amine solution, amines do not behave in this manner. When the chemical bond between the amine and the acid gas is formed, it is not easily broken. Attempts to desorb the acid gases by pressure reduction, gentle heating, or gas stripping will therefore have only limited success. The only way to release significant amounts of acid gas from the amine solution is to break the chemical bond by vigourous steaming of

10   the solution in the amine regenerator. Some proposed process schemes are based on mild partial regeneration to create a semi-lean amine solution, which, because it is supposedly already loaded with CO_2, will resist further absorption of CO_2, and absorb H_2S instead. Such schemes have proven impractical.

SUMMARY OF THE PRESENT INVENTION

The process of the present invention recognizes that coabsorption of CO_2 and H_2S by tertiary amines is essentially unidirectional and that, short of vigorous regeneration of the rich solution by steaming, desorption of acid gas from rich solution is not significant.

5   Absorption responds to partial pressures, solution loading, and temperature. However, because the chemical bond formed during absorption cannot be easily broken, in practical situations desorption will not respond to these measures.

The present process is most applicable to situations where the CO_2/H_2S ratio in the natural gas (indicated by reference numeral 10 in figs. 4 to 7) that feeds into the plant

10   is relatively high. In this scenario, a rich amine solution exiting the high pressure absorber would therefore also have a relatively high ratio of CO_2 to H_2S, even if CO_2 slipping was used. In addition, because regeneration strips essentially all of the acid gas from the solution, the regenerator overhead vapour in a conventional MDEA plant would also have a high CO_2 to H_2S ratio. This invention proposes to improve this ratio by

15   recycling an acid gas slip stream, which is rich in H_2S, to contact the rich amine prior to regeneration where, because of the higher partial pressure of H_2S in the recycled acid gas, further absorption of H_2S into the rich solution can occur. The source of the H_2S enriched acid gas is the overhead vapour from the regenerator. If a sufficient portion of this overhead vapour is recycled, the rich amine solution will be enriched in H_2S and,

20   since the regeneration process strips essentially all acid gas from the rich solution, the

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regenerator overhead vapour will also be H_2S-enriched. A portion of this enriched overhead vapour is recycled back to enrich the amine solution, and the entire system will come to a new dynamic equilibrium based on these new conditions, resulting in regenerator overhead vapours having a significantly higher proportion of H_2S over CO_2.

In summary, the following process concepts form the basis of the invention.

(1) Tertiary amines exhibit a preferential affinity for H_2S over CO_2 primarily because of differing rates of absorption. Therefore, when H_2S and CO_2 are coabsorbed from gases, the relative proportion of H_2S to CO_2 in the amine will be higher than the corresponding proportion in the gas phase. This is because in the actual processing equipment H_2S is absorbed more rapidly than CO_2.

(2) Absorption of acid gas by amine involves physical absorption plus chemical reaction. Absorption occurs readily, but desorption to separate the acid gas from the amine is much more difficult because the reaction that bonds the acid gas chemically to the amine is not easily reversed except by intense steaming at elevated temperature. Mass transfer of acid gas is therefore essentially unidirectional throughout most of the process except for the regeneration where the chemical bond that links acid gas to amine is broken by steaming the rich solution. After regeneration the amine is totally stripped of all acid gas except for very minor residual amounts.

(3) Rich tertiary amine in contact with sour gas will be loaded with both H_2S and CO_2 in proportions dictated by the ratio of H_2S to CO_2 in the gas phase, by the contact time

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and by the conditions of contact. While the rich solution does not readily give up its acid

gas short of vigorous regeneration, it is possible to more fully load the rich solution with

H_2S when the solution is in contact with a gas which is enriched with H_2S when the

solution is in contact with a gas which is enriched with H_2S at the proper operating

5   conditions.

(4)   If the tertiary amine is initially contacted with gas that is relatively lean in H_2S but

rich in CO_2, the H_2S will be totally absorbed, but a portion of the CO_2 will remain

unabsorbed and will not be removed from the gas. This is referred to as "slipping" a

portion of the CO_2. If the rich amine from the first contact is then contacted with the

10   second gas that is richer in H_2S than the first gas, then the rich amine is capable of

absorbing additional H_2S from the second gas, provided that concentrations and operating

conditions are favourable.

However, the rich amine which contacts the second gas is not capable of totally

removing the H_2S from the second gas because it is already partially loaded with H_2S.

15   Equilibrium conditions between the rich amine and the second gas will permit only

partial absorption of the H_2S, but will not permit total removal. Thus, while slipping CO_2

from the second gas, a portion of the H_2S will also be unavoidably slipped while in

contact with the rich amine. In order to pick up the slipped H_2S from the second gas, the

second gas must be contacted with lean amine which is sufficient to absorb the H_2S but

20   will continue to allow the CO_2 to slip. The second gas, after being contacted by both rich

and lean amine streams, will consist of substantially pure CO_2 after all the H_2S is removed.

(5)   Based on the principles described in (4) above, it is possible to extend the enrichment method by devising a multistage enrichment system wherein the acid gas is

5   progressively enriched in stages by contacting rich amine with recycled acid gases that are progressively richer in H_2S in a series of absorbers and regenerators.

(6)   It is possible to realize some reduction in process heat requires for regeneration of the rich amine solution by tailoring the acid gas residuals contained in the lean solution to suit the requirements of the individual absorbers. Absorbers with an extreme intolerance

10   for acid gas residuals would be drawn from the bottom of the regeneration column where it would be exposed to the most intense degree of steaming. Absorbers with a greater tolerance for acid gas residuals could draw their lean amine from an intermediate stage in the column where the degree of regeneration heat is less. Overall, the two lean streams require less process heat than producing a single lean stream with very low residuals.

15   The above described principles recognize the physical and chemical nature that is inherent in tertiary amines. By employing these principles in combination it is possible to devise a process that should greatly enrich the H_2S concentration of the acid gas feed to a sulphur plant. It should also produce a secondary benefit of producing a side stream of essentially pure CO_2 which may also have commercial value.

20

BRIEF DESCRIPTION OF THE DRAWING FIGURES

Embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawings, wherein:

5   Figure 1 illustrates a carbamate reaction of an amine and carbon dioxide;

Figure 2 illustrates a series of CO_2-tertiary amine reactions resulting in a positively charged amine-hydrogen ion;

Figure 3 shows a typical prior art amine process employing a primary absorber and regenerator;

10   Figure 4 shows a simple acid gas recycle process according to one embodiment of the present invention;

Figure 5 shows a "single effect" acid gas enrichment process according to another embodiment of the present invention; and,

Figure 6 shows a "single effect" process with a lean/superlean system according to

15   a further embodiment of the present invention; and,

Figure 7 shows a "double effect" acid gas enrichment process according to yet another embodiment of the present invention.

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DESCRIPTION OF PREFERRED EMBODIMENTS

In one embodiment of the present invention shown in figure 4 the process recycles acid gas vapours back to the mid-point of a high pressure amine absorber for the purpose of increasing the concentration of H_2S in the amine solution exiting the base of the

5   column. The introduction of additional H_2S into the absorber column, however, means that conditions in the upper sections of the column must be altered in order to maintain H_2S specifications on the product gas while slipping additional CO_2. Hence, this embodiment is not as practical as the other embodiments described below.

In a second more practical embodiment of the present invention shown in fig.5,

10   the process, sometimes referred to herein as a "single effect process", uses a second absorber column (indicated by reference numeral 30) which operates at a pressure that is intermediate that of the main high pressure absorber tower 20, also referred to herein as the "first absorber", and the low pressure amine regenerator 40. Acid gas that is enriched in H_2S is fed into the base of the second absorber column at 38 where it comes in contact

15   with rich amine from the high pressure absorber 20 (which enters the second column 30 at 32) in counter-current flow over a series of contact stages in the second absorber 30. While the amine solution picks up additional H_2S, CO_2 loading remains relatively unchanged, resulting in a rich stream exiting from the base of the second column at 34 that has been enriched in H_2S. Vapours rising above the feed tray, where rich amine from

20   the high pressure absorber enters the second absorber at 32, will be in contact with a

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solution that is already significantly loaded with acid gas. As a consequence, these vapours will contain both H_2S and CO_2. In order to achieve a useful separation in the second column 30, it is necessary to eliminate essentially all of the H_2S from the overhead vapour so that it can either be disposed of, or marketed as an essentially pure

5   CO_2 stream 31. This should be accomplished by introducing a lean stream of tertiary amine at 36 directly from the amine regenerator 40 onto the top tray of the second absorber. Because of its low residual concentration of acid gas, the lean stream should reduce the H_2S in the overhead gas essentially to zero in the second absorber, leaving an overhead of essentially pure CO_2 and water vapour, plus whatever non-condensible

10   hydrocarbons were dissolved in the rich amine solution from the high pressure absorber 20.

The second column 30 has three feeds. Lean amine enters at the top of the column at 36, while rich amine from the high pressure absorber 20 enters at the midsection of the column at 32, while recycled acid gas enters at the column's base at 38.

15   The overhead vapour stream 31 – one of two streams leaving the second absorber – consists mostly of CO_2 and water. The bottom liquid stream at 34 consists of rich amine enriched with H_2S. The lean amine stream 36 entering at the top of the column contacts the rising acid gas vapours counter-currently through several stages of contact where it preferentially absorbs H_2S, and allows a substantial portion of the CO_2 to slip past

20   unabsorbed until it exits at the top 31 of the second column. At the rich amine feed stage

at the mid-section 32 of the absorber, the lean stream 36, now partially loaded with acid gas, flows from the upper section of the column and blends with the incoming rich amine feed. As the blended amine stream flows downward through the lower section of the second absorber, it preferentially absorbs H_2S from the acid gases before exiting from the base 34 of the column.

In another aspect of the present process a flash tank 50 may be added to the system by locating it between the high pressure absorber 20 and the second absorber 30. The tank's purpose is to flash off non-condensible vapours, namely principally methane and ethane, which are picked up in small quantities in the high pressure absorber where the amine acts as a physical solvent for hydrocarbons. These hydrocarbons are largely flashed off in the flash tank, along with minor amounts of H_2S and CO_2. This flash vapour, exiting at 52, can also be sweetened and used as plant fuel. The purpose of the flash tank is to remove non-condensible vapours that would otherwise appear in the overhead vapour 31 from the second absorber 30, contaminating the CO_2.

The present invention is based on recycling a portion of the overhead acid gas stream from the regenerator 40 for the purpose of improving the ratio of H_2S to CO_2 in the acid gas stream 12 going to the sulphur plant. Carbon dioxide, which is an undesirable contaminant in the sulphur plant, is excluded at two points in the process. First, the CO_2 is only partially absorbed in the high pressure absorber 20, allowing a portion of the CO_2 to slip and remain in the residue gas, namely the "sweet gas" 14.

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Second, CO_2 is separated from the rich amine in the second absorber 30, where it is removed overhead at 31 as essentially pure CO_2 and water. When the overall plant material balance for CO_2 is calculated, the concentration of H_2S in the overhead stream 41 from the regenerator 40 should be greatly increased, significantly improving its quality as a sulphur plant feed and improving the conversion of H_2S to sulphur in the sulphur plant.

Lean tertiary amine that leaves the regenerator 40 is split into two streams, namely a first stream 43 which flows to the top of the high pressure absorber 20, and a second stream 36 which flows to the top of the second absorber 30. The first stream 43 is sufficient to produce a sweet natural gas product, and the second stream 36 is used to sweeten recycled acid gas for the purpose of improving H_2S concentration in the feed 12 to the sulphur plant. This internal recycle system consisting of recycled enriched acid gas 38 requires additional lean amine 36, additional heat to regenerate the additional amine, and additional pumping and acid gas compression at 46 to recycle the internal streams. With this approach, additional process costs will be incurred in improving the H_2S/CO_2 ratio of the acid gas 12 leaving the plant, but these costs are reasonable and practical for most systems. However, with very lean streams, the acid gas ratio in the rich amine 21 from the high pressure absorber 20 will become increasingly unfavourable, and a greater and greater portion of the overhead regenerator vapour 41 must be recycled in order to gain a significant improvement in the concentration of H_2S in the acid gas stream 12

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leaving the plant. In this case, the recycle stream 38 and the lean amine stream 36 going to the second absorber 30 become the dominant elements in the plant, resulting in potentially excessive process costs for reabsorbing and regenerating recycled streams.

Lean/Super Lean Amine Systems

5   It has been stated that in order to remove virtually all of the H_2S from a sour gas stream 10 while allowing a portion of the CO_2 to slip through an absorber, the lean amine solution must be stripped in a regenerator to a very low residual H_2S content. An H_2S content of 0.0015 mole percent is a typical H_2S residual for lean 50% (weight) MDEA. If residual H_2S rises much above this level, the H_2S content in the gas exiting the top of the

10   absorber will exceed acceptable limits. It has been found that the high pressure absorber 20 is much more tolerant of residual H_2S than the low pressure secondary absorber 30, even though the specification for H_2S in the gas from the high pressure absorber is much tighter than the specification for the low pressure absorber. The high pressure absorber can tolerate more residual H_2S because it has a much higher partial pressure driving force

15   to cause H_2S to diffuse through the gas film at the liquid interface and into the body of the amine liquid. The low pressure absorber must function with a much lower H_2S partial pressure in the gas phase at the top of the column with the result that even modest amounts of residual H_2S in the lean amine inevitably create such resistance to diffusion that final traces of H_2S will not be absorbed and significant amounts of H_2S will break

20   through with the gas exiting from the top of the second absorber.

In order to meet the strict requirements for low residual H$_2$S in the lean amine

entering the second absorber 30 (which operates at a lower pressure than the first absorber

20), it is necessary to create a super lean amine by expending extra heat energy in the

regenerator. The first absorber requires low residual H$_2$S, but because of its higher

5   operating pressure, can tolerate residuals which are typically about five to ten times

higher than those required for the low pressure absorber. Moderate steam stripping in the

regenerator 40 is adequate to produce lean amine for the high pressure absorber, but for

the low pressure second absorber intense steam stripping is necessary to produce a super

lean tertiary amine having the required extremely low residual H$_2$S content. In a simple

10   system, the single bottom product leaving the amine regenerator has been stripped of H$_2$S

to the level necessary to meet the needs of the low pressure absorber, even though the

high pressure absorber can tolerate a much higher level of H$_2$S residual in the lean

solution.

The different requirements for lean amine purity for the two absorbers suggest an

15   alternate arrangement for regenerating the amine solution. Instead of drawing all of the

lean amine from the base of the regenerator still column, the lean amine for the high

pressure absorber can be drawn from an intermediate tray approximately five stages

above the reboiler 45 located at the base of the column. The portion of lean amine drawn

from the intermediate tray will have residual H$_2$S low enough to meet the needs of the

20   high pressure absorber, while the balance of the amine remaining in the regenerator still

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column will continue to downflow over the trays in the lower section of the column where it is subject to the intense steaming necessary to regenerate a super lean solution suitable for the low pressure absorber. The two draw-off points in the still column serve to reduce the overall process heat necessary to regenerate the solution. Instead of expending the energy required to regenerate the total amine solution to the standard of purity required by the low pressure absorber, a lesser amount of energy is expended to regenerate a conventional lean amine for the high pressure absorber, plus a super lean stream for the low pressure absorber. This lean/super lean system is a relatively simple enhancement to the process that will improve overall energy efficiency.

The flow scheme for the lean/super lean system is illustrated in fig.6. In this third embodiment of the invention there are two amine streams exiting from the regenerator, namely a lean steam and a super lean stream. The lean stream 44 is drawn from an intermediate stage in the regenerator 40 that is several stages above the reboiler 45 but is below the feed stream 34 which comes from the second absorber 30. After leaving the regenerator, the lean stream 44 is cooled by flow through the rich/lean exchanger and the lean cooler after which it enters the first absorber as stream 43.

The super lean stream 42 exits from the bottom of the regenerator 40 in a customary manner and is pumped through the rich/super lean exchanger and the super lean cooler after which it enters the second absorber 30 as stream 36.

Extremely Lean Acid Gas

For extremely lean streams where, for example, the molar ratio of H_2S to CO_2 in the rich amine stream from the high pressure absorber is 1% or less, yet another, or fourth, embodiment of the invention shown in fig.7 should be considered. Low molar

5   ratios exist where, for example, H_2S in the natural gas is 0.03%, while CO_2 is 5%. In spite of slipping CO_2 in the high pressure absorber, there will be a very strong predominance of CO_2 in the rich amine with a typical H_2S/CO_2 ratio of 1% or less. A 1% H_2S/CO_2 ratio as feed to a Claus sulphur plant following a conventional amine plant would be literally impossible to operate. Using the second embodiment of the invention

10   (i.e. the single effect system) as described above, the H_2S/CO_2 ratio in the acid gas could be increased by a factor of about 5, or from 1% to 5%.

In applying the second embodiment of the invention to a system that is very low in H_2S, the acid gas recycled to the second absorber is still a comparatively lean gas, even though the H_2S has been concentrated by, for example, a factor of five. As the proportion

15   of acid gas recycled is increased, the gain in concentrations of H_2S appears to approach a limit beyond which the amount of process energy expended becomes impractical. In this case, H_2S/CO_2 ratio can only be improved by employing the second embodiment of the invention, namely a double effect system shown in fig.7.

Whereas the second embodiment of the invention may be referred to as a "single

20   effect system", the fourth embodiment of the system may be referred to as a "double

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effect system", which involves coupling together two stages of low pressure absorption and regeneration. Components of the system in fig.7 which are the same or similar to those shown in fig.4 are identified with the same reference numerals, except with the addition of a prefix "1". The double effect system consists of all the basic component

5   parts of the single effect system, including the high pressure absorber 120, the optional flash tank 150, the second absorber 130, the regenerator 140, a compressor146 to recycle acid gas, and a means of pumping lean amine to the two absorbers. The double effect system adds to the basic system a third absorber tower 160, a second regenerator 170, an additional lean amine pump 180, and an acid gas compressor 190.

10   The double effect system attaches directly to the acid gas outlet 112 from the single effect system. The acid gas enters at the base 161 of the third absorber 160 , along with H_2S enriched acid gas at 162 recycled from the overhead 171 of the second regenerator 170. Lean amine from the second regenerator is divided into two streams: one stream 173 flows to the top of the third absorber at 163; and a second stream 174,

15   which combines with lean amine from the first regenerator 140, flows to the top of the first absorber at 122.

In the double effect system, greater concentrations of H_2S are achieved by rejecting a stream of essentially pure CO_2 and water overhead from the third absorber at 164. This CO_2, which is rejected from the process, may be combined with CO_2 from the

20   second absorber 130. The second effect should improve upon the first effect's H_2S/CO_2

ratio by approximately a factor of three. The overall improvement in the ratio is therefore the product of the improvement in the first and second effects, which in the example cited is the product of 5 and 3. (If acid gas from the first effect has the H_2S/CO_2 ratio improved by a factor of 5, the overall ratio improvement leaving the second effect will be

5   15.) Thus, a H_2S/CO_2 ratio of only 1% should be improved to 15% in stream 172 by the use of a double effect system. A ratio of 15%, while still a relatively lean acid gas, is a practical concentration of H_2S for feed to a Claus sulphur plant. Individual cases will obviously vary, with final concentrations depending on initial concentrations, and the degree of recycling employed in the process.

10   The above description is intended in an illustrative rather than a restrictive sense, and variations to the specific configurations described may be apparent to skilled persons in adapting the present invention to other specific applications. Such variations are intended to form part of the present invention insofar as they are within the spirit and scope of the claims below. For instance, it will be appreciated that the present process

15   may be extended to a third effect or more, increasing the concentration of H_2S at each stage. For each succeeding effect, the feed into the low pressure absorber would be the acid gas produced by the preceding effect.
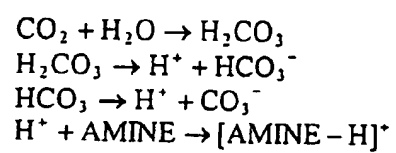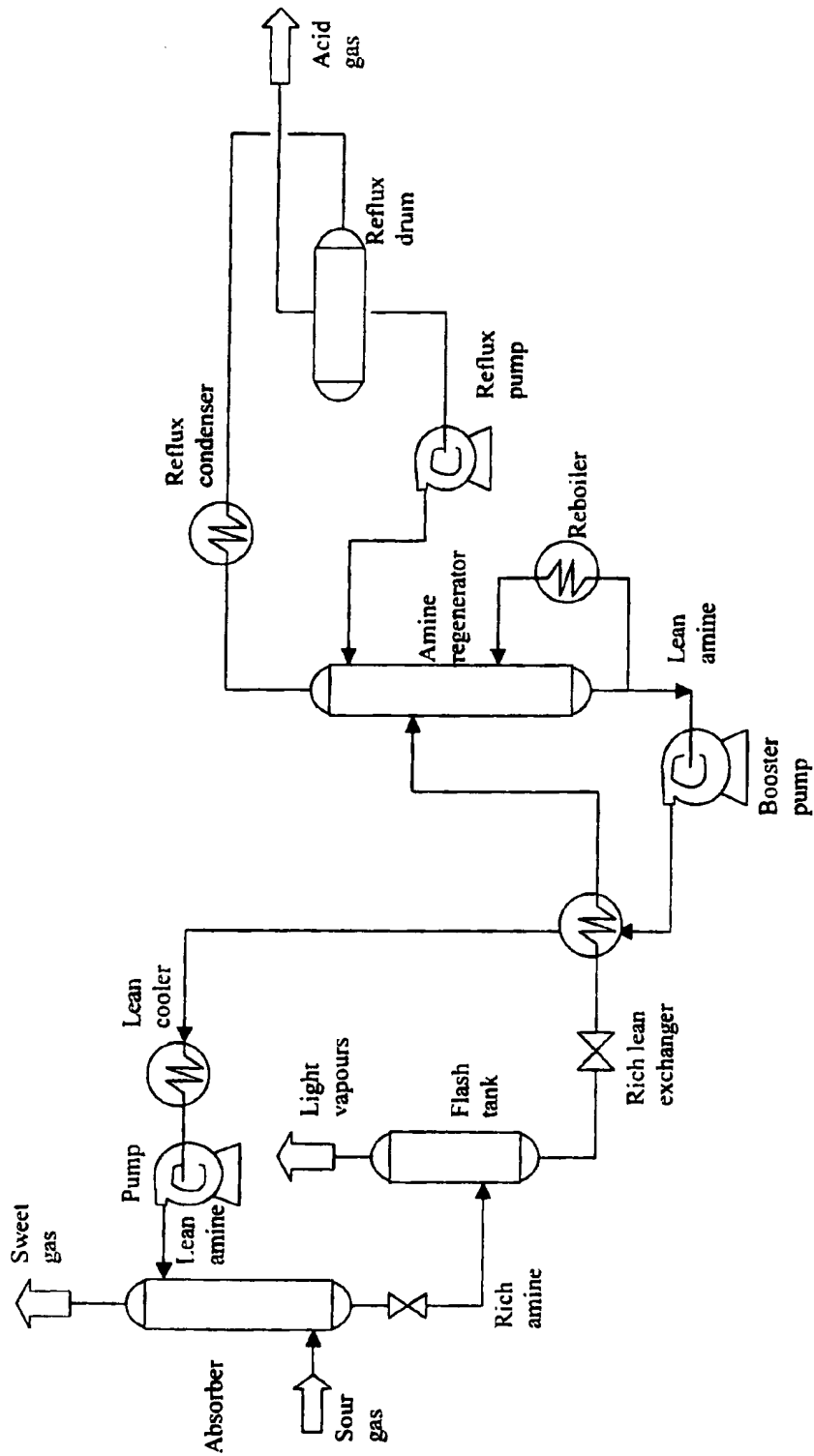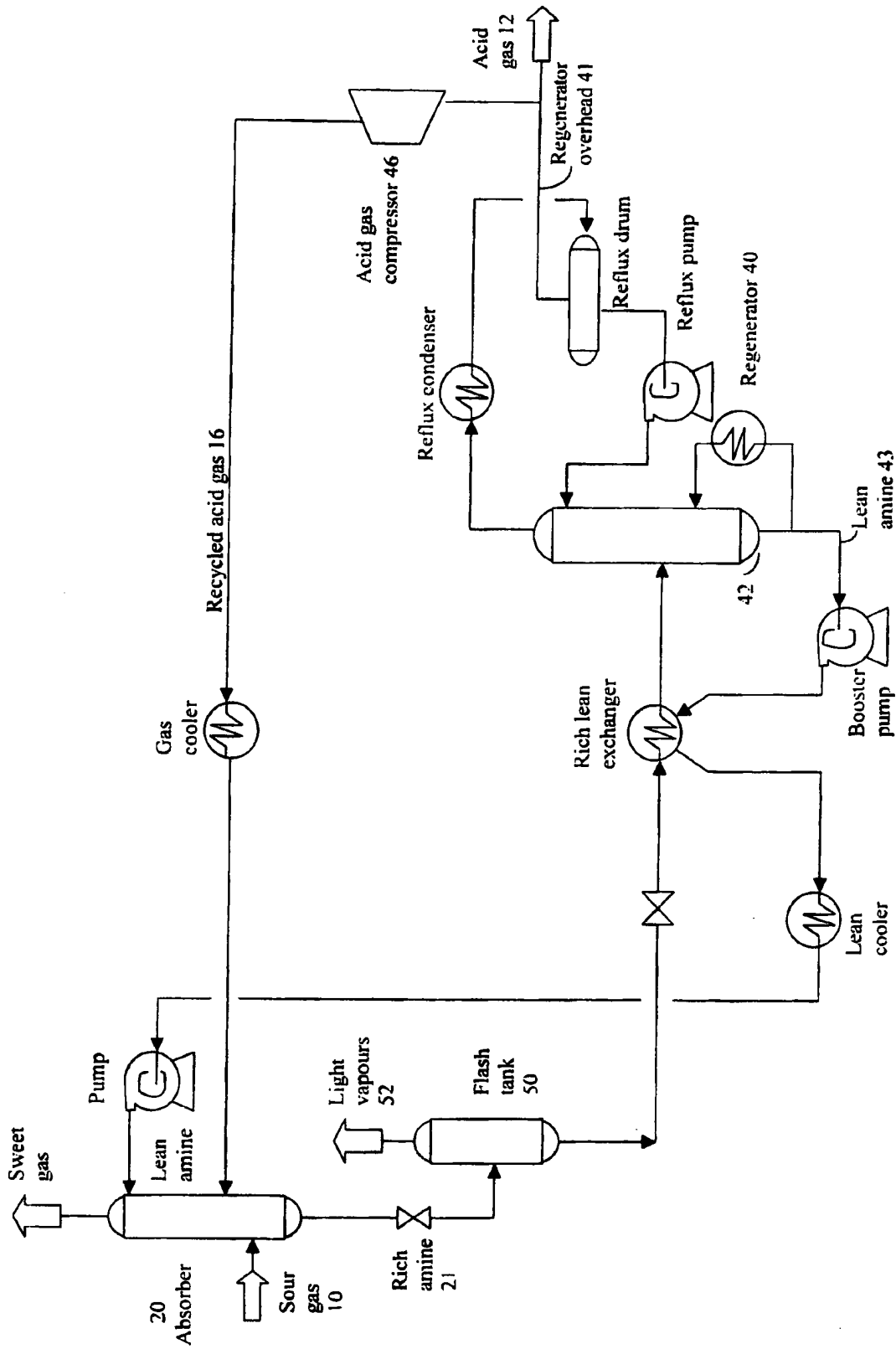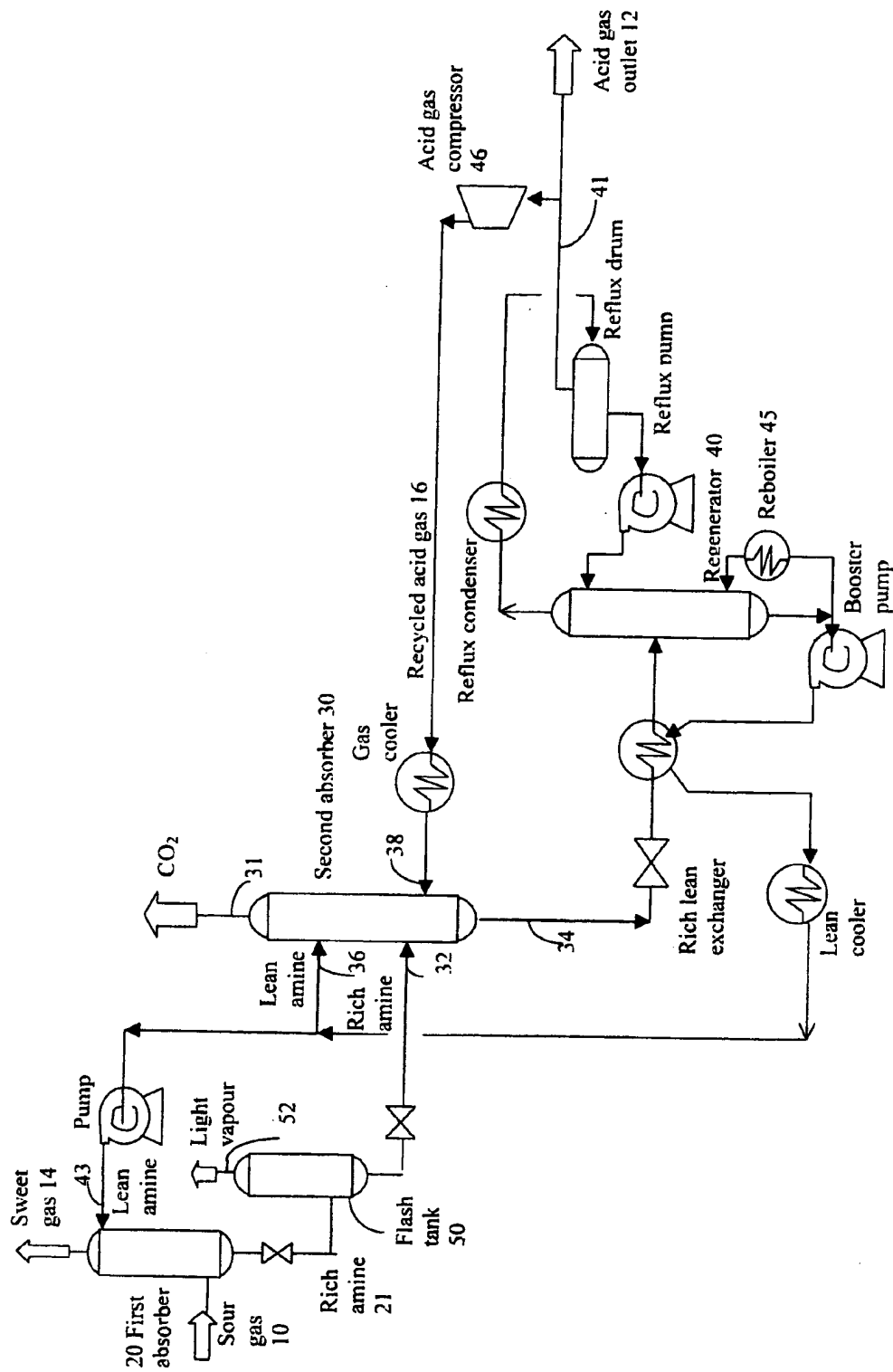
20

Figure 1

$$CO_2 + AMINE \rightarrow [AMINE]^+ + [AMINE - \overset{\overset{\displaystyle H}{\overset{\displaystyle |}{\underset{\displaystyle |}{O}}}}{C} - O]$$

$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$H_2CO_3 \rightarrow H^+ + HCO_3^-$$
$$HCO_3 \rightarrow H^+ + CO_3^-$$
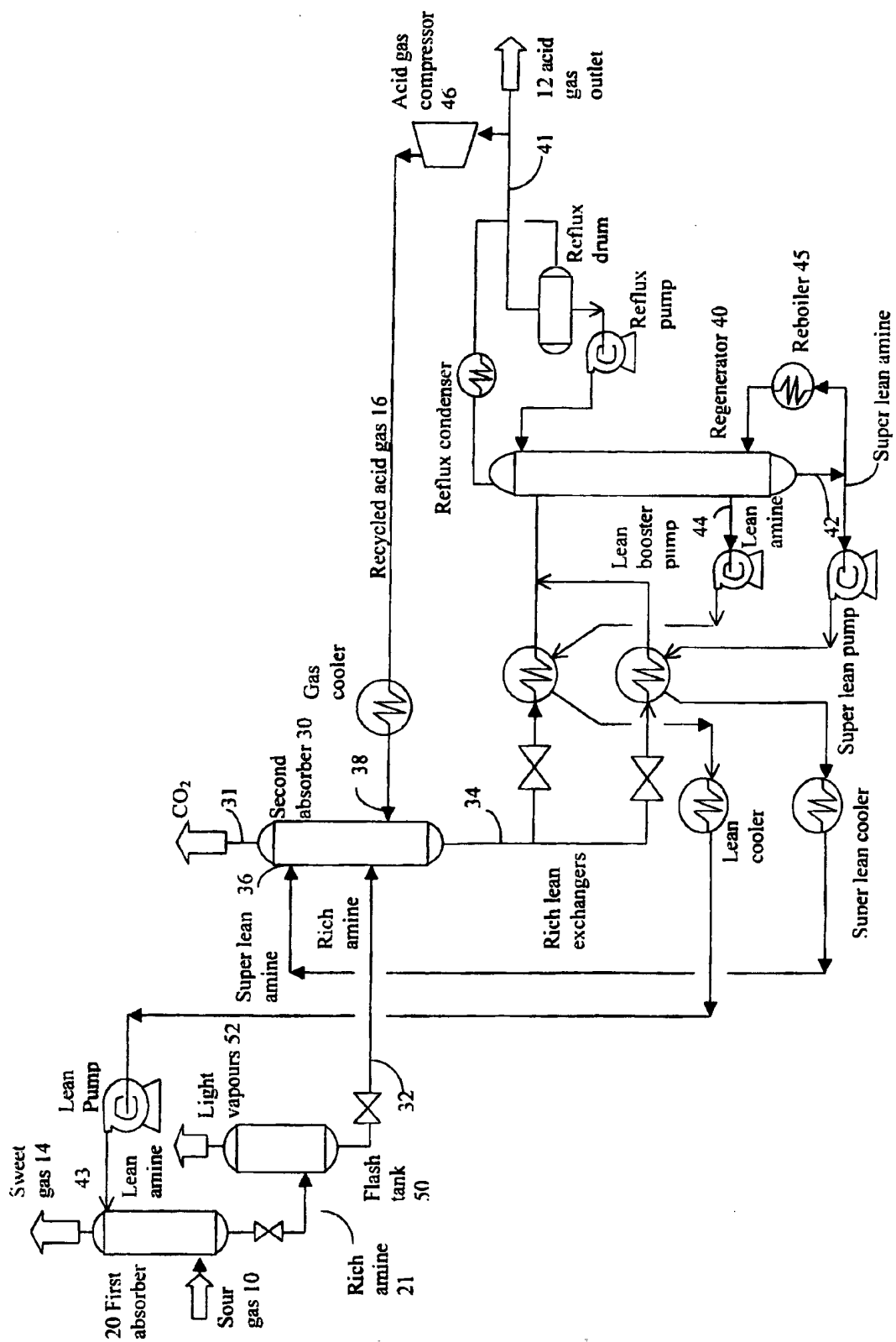$$H^+ + AMINE \rightarrow [AMINE - H]^+$$

Figure 2

Typical Standard Amine Process (Prior Art)
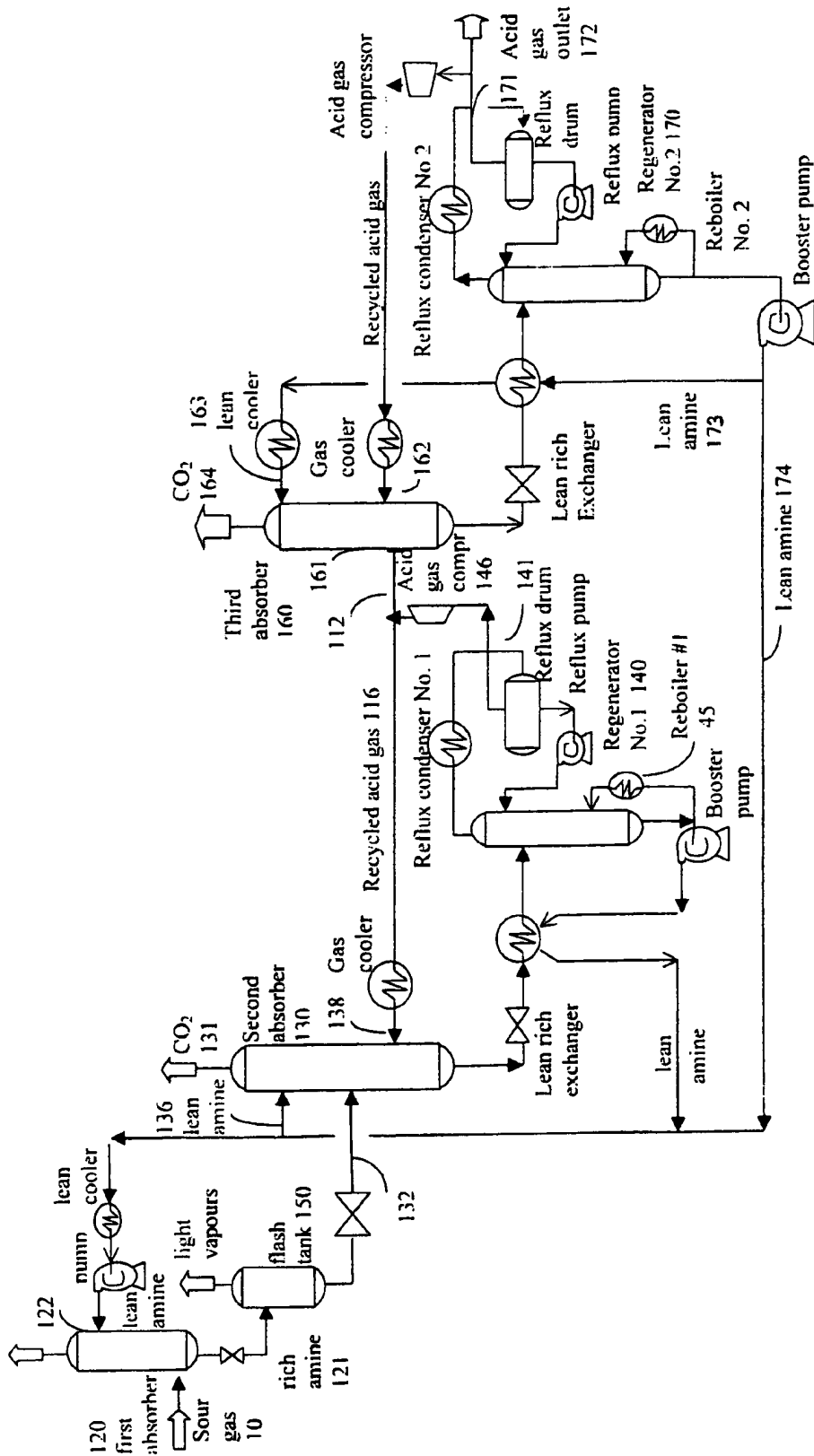FIGURE 3

Simple Acid Gas Recycle Process
FIGURE 4

Single Effect Process
FIGURE 5

Single Effect Process With Lean/ Superlean System

FIGURE 6

Double Effect Process
FIGURE 7